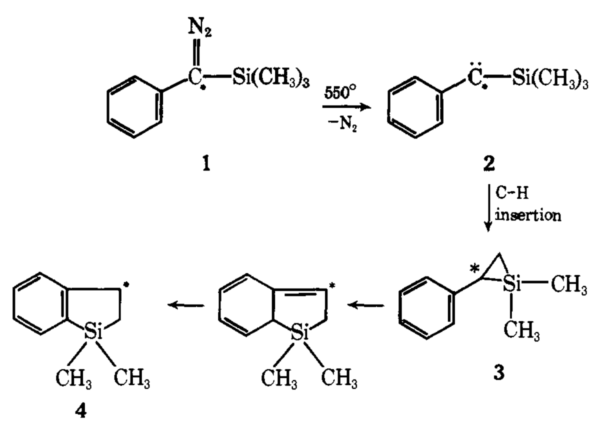
Scheme I

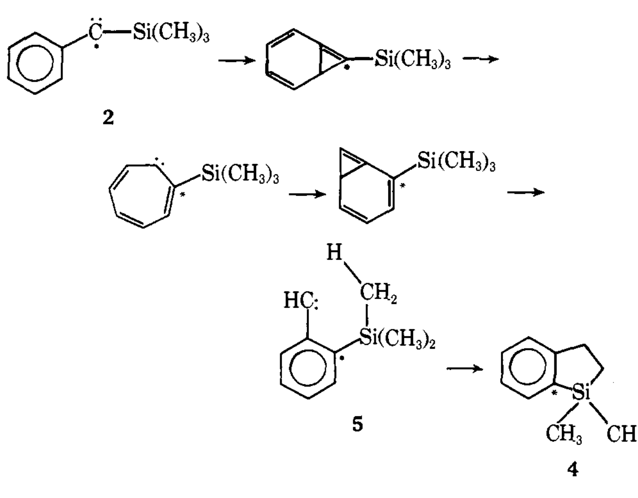


and coworkers[2] reported that the gas-phase pyrolysis (550°, N_2 flow) of phenyltrimethylsilyldiazomethane (**1**) afforded benzosilacyclopentene (**4**) and that this product was evidence for the intermediacy of silacyclopropane (**3**), which resulted from the intramolecular insertion of carbene **2** into a C-H bond of a methyl group (Scheme I).

We had previously observed the formation of **4**, and rationalized it in terms of quite a different mechanism. We considered the precursor to **4** to be the carbene **5**, itself formed by a well-precedented sequence of steps involving carbene-to-carbene rearrangements[3] (Scheme II). Carbene **5** can lead to **4** by a straightforward insertion into a carbon-hydrogen bond.

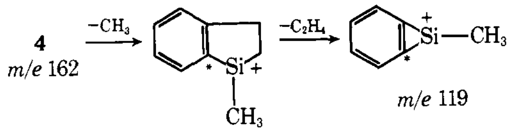
A method of distinguishing between these two mechanistic pathways is obvious once it is noted that the benzylic carbon of **1** remains aliphatic in the Ando mechanism (Scheme I) but becomes the aromatic carbon bonded to silicon in the carbene-interconversion mechanism (Scheme II). Phenylmagnesium bromide was converted to ^{13}C labeled benzoic acid with labeled CO_2 and then to labeled **1** by the procedure of Brook and Jones.[4] Mass spectrometric analysis of the intermediate tosylhydrazone indicated a 24.3% ^{13}C content. Thermal decomposition of labeled **1**, carried out in the inlet port of the preparative gas chromatograph at 300°, afforded **4**. Comparison of the ^{13}C nmr spectra of labeled and unlabeled **4** revealed *no* enhancement of the three aliphatic carbon absorptions (31.81, 11.47, and −1.59 ppm from TMS) and hence no incorporation of ^{13}C into the saturated carbons of the five-membered ring. The absorption of only one aromatic carbon (139.86 ppm from TMS) was enhanced by an average factor of 19.7 over the other aromatic carbon absorptions.

Scheme II



A second sample of **4** was prepared independently by the flash pyrolysis (420° (0.5 mm)) of the lithium salt of the tosylhydrazone of phenyltrimethylsilyl ketone. The ketone was prepared from ^{13}C labeled methyl benzoate (12.8%) by the method of Picard, *et al.*[5] In this case an average enhancement of 13-fold was observed for the same aromatic absorption as was found previously in the decomposition of the diazo compound.

The conclusion that the labeled carbon is now in the aromatic ring is further confirmed by a comparison of the mass spectra of the labeled and unlabeled benzosilacyclopentenes (**4**). The fragmentation of **4** proceeds through loss of a methyl group and then the loss of C_2H_4 (there is no metastable peak for the C_2H_4 loss, so the concertedness of the process is unknown) to yield an ion of the composition C_7H_7Si (*m/e* 119.03185 ± 0.0006, calcd 119.0317). Comparison of the m/e 162/163 and 119/120 intensity ratios indicated a ^{13}C content of 24.8% in the parent ion with 23.6% in the fragment ion. Thus, within reasonable experimental error limits, all of the extra ^{13}C remained with the aromatic fragment.



In summary, the thermal conversion of **1** to **4** does not involve a silacyclopropane but rather provides a further example of the phenylcarbene-cycloheptatrienylidene interconversion.

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Crystal Structure of 5,6,11,12-Tetradehydrodibenzo[*a,e*]cyclooctene (*sym*-Dibenzo-1,5-cyclooctadiene-3,7-diyne)

Sir:

We report the results of a single-crystal X-ray structure determination on the recently described[1] 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**1**). The only other previously known compound with two triple bonds in the eight-membered system is 1,5-cyclooctadiyne (**2**), for which only

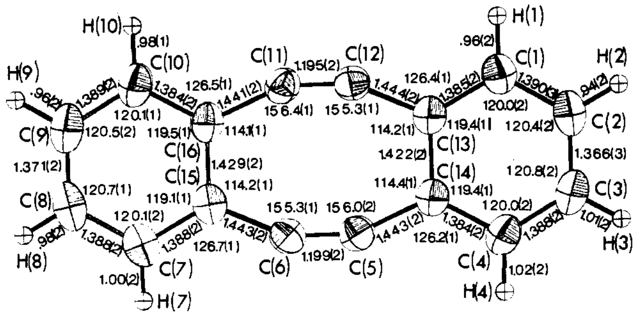

Figure 1. The molecule seen along the direction corresponding to the maximum moment of inertia. The carbon atoms are represented[8] by temperature-factor ellipsoids drawn at the 40% probability level. Hydrogen atoms are on an arbitrary scale.

preliminary structural data are available.[2] The present study provides evidence that the conjugated eight-membered ring of **1** in the crystalline state is substantially planar, the slight deviation from planarity being probably due to intermolecular effects.

Crystals of **1** suitable for diffraction work could be grown from a tetrahydrofuran solution. The compound crystallizes in the monoclinic system with the following unit cell constants: $a = 6.144$ (1), $b = 11.840$ (1), $c = 14.031$ (1) Å; $\beta = 91.01$ (1)°; space group $P2_1/n$; $Z = 4$; $\rho_{\text{calcd}} = 1.302$ g cm^{-3}; μ(Cu Kα) = 5.75 cm^{-1}. The density was not measured, due to the paucity of the substance in our hands after crystallization. A complete set of diffraction maxima within a θ sphere of 70° was measured with a fully automated four-circle diffractometer using Cu radiation [λ(Cu Kα) = 1.5418 Å; graphite monochromator] and a variable rate θ-2θ scan technique. A single standard check reflection was measured after every 15 reflections; a general downward trend in the intensity of this reflection was observed, the intensity drop at the end of the data collection amounting to 10%. Of the 1910 reflections measured a total of 1775 were judged observed after correction for Lorentz, polarization, background, and decay effects. The structure was solved by automated interpretation[3] of the Patterson function. Least-squares refinement using anisotropic thermal parameters for carbon atoms, isotropic temperature parameters for hydrogen atoms, an overall scale factor, and a secondary extinction parameter[4] gives a value of the conventional R index[5] of 0.048 and a weighted R index[6] of 0.050. The refined atomic coordinates are given in Table I;[7] observed and calculated structure factors are listed in Table II.[7]

A drawing of the molecule is shown in Figure 1, which includes bond distances and angles involving C atoms and C-H distances.[8] For sake of clarity the values of the C-C-H angles have not been reported; they range between 118 and 121° (esd's = 1°).

Four structural features are of special note. (1) The average value of the angles at carbon atoms involved in triple bonds is 155.8° (to be compared with a value of 159.1° in **2** and of 158.5° in cyclooctyne[9]). (2) The distance between the triple bonds is 2.61 Å (against 2.57 Å in **2**). (3) Atoms C(5), C(6), C(11), and C(12) are coplanar within 0.001 Å (plane A); the displacements of the other four atoms of the eight-membered ring from plane A range between 0.014 and 0.023 Å, all in the same direction. (4) The two outer benzene rings are planar within experimental uncertainty (maximum deviation 0.003 Å); their planes are both folded out of plane A, on the same side, by about 2°. This folding, and the consequent nonstrict planarity of the central ring, can presumably be ascribed to packing interactions. Among these, we notice a rather short contact of 3.45 Å, which involves atom C(1) and atom C(8) of another molecule at $1 - x, -y, 1 - z$; a less critical contact of 3.54 Å implicates atom C(14) of the first molecule and atom C(10) of the molecule transformed as for C(8).

Acknowledgments. The authors feel especially indebted to Professor F. Sondheimer, who kindly supplied them with the crystal specimens prior to the publication of his paper.[1]

Supplementary Material Available. A listing of final atomic parameters and structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-658.

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Correlation between Proton Affinity and Core-Electron Ionization Potentials for Double-Bonded Oxygen. Site of Protonation in Esters

Sir:

A striking correlation of the proton affinities of a number of alcohols and amines with the core-electron ionization potentials of oxygen or nitrogen in the same molecule has been pointed out by Martin and Shirley[1] and by Davis and Rabalais.[2] The change in proton affinity from one molecule to another is almost exactly equal to the change in core ionization potential. The reason for this result is that the removal of a core electron from the oxygen or nitrogen is electrically equivalent to the addition of a proton at the same site. It was suggested by Martin and Shirley that the ionization-potential shifts and proton affinities might be comparable over a wider range than they had considered.

Davis and Rabalais found, however, that the point for acetone fell off of their correlation line by about 1 eV and that the point for formic acid was off by nearly 0.5 eV. They concluded, therefore, that double-bonded oxygen does not fit the correlation and proposed a number of reasons to account for the phenomenon.

We have recently remeasured the oxygen 1s ionization potential in acetone to be 537.92 eV, in substantial disagreement with the previously reported value of 539.0 eV.[3] Our new value falls quite close to the correlation line for the alcohols. In addition, we have measured oxygen 1s ionization potentials for methyl acetate (537.87 and 539.43 eV), formaldehyde (539.42 eV[4]), and acetaldehyde (538.62 eV[5])